

## 中华青英叶的一个新果糖酯\*

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**摘要:** 从山茱萸科中华青英叶 (*Helwingia chinensis*) 的乙醇提取物中分离得到一个新果糖酯和十个已知化合物。通过现代波谱技术分别鉴定为: 2-*O*-(*E*)-咖啡酰-3-*O*-(3, 5-二甲氧基香豆酰)- $\beta$ -D-呋喃果糖甙 (1), 2-*O*- $\beta$ -D-呋喃果糖基- $\beta$ -D-异吡喃糖酯 (2), 甘草甜素 (3), 4-羟基-7-*O*-葡萄糖-2, 3-二羟黄酮甙 (4), 黄豆甙 (5), 5-葡萄糖芹菜甙 (6), 7-*O*-葡萄糖芹菜甙 (7), 4-*O*-葡萄糖香豆酸 (8), 葡萄糖咖啡酸 (9), 3-赤杨醇 (10), 薯蓣皂甙 3-*O*-{ $\beta$ -L-鼠李糖吡喃糖基 (1 $\rightarrow$ 2)-[ $\beta$ -L-阿拉伯呋喃糖基 (1 $\rightarrow$ 3)]- $\beta$ -D-葡萄糖吡喃糖} (11)。

**关键词:** 中华青英叶; 山茱萸科; 呋喃果糖; 黄酮甙; 抗菌活性

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## A New Fructofuranoside from *Helwingia chinensis* (Cornaceae)

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**Abstract:** A new fructofuranoside, together with ten known compounds were isolated from the EtOH extraction of the aerial part of *Helwingia chinensis*. Their structures were elucidated to be 2-*O*-(*E*)-caffeoyl-3-*O*-(3, 5-dimethoxycoumaroyl)- $\beta$ -D-fructofuranose (1), 2-*O*- $\beta$ -D-fructofuranosyl- $\beta$ -D-allopyranose (2), liquiritigenin (3), 4-hydroxy-2, 3-dihydro-flavonone-7-*O*- $\beta$ -D-glucoside (4), daidzin (5), apigenin 5-*O*-glucopyranoside (6), apigenin-7-*O*- $\beta$ -D-glucoside (7), coumaric acid 4-*O*- $\beta$ -D-glucopyranoside (8), glucopyranosylcaffeic acid (9), 3-hydroxyglutin-5-ene (10), diosgenin 3-*O*- $\beta$ -L-rhamnopyranosyl (1 $\rightarrow$ 2)-[ $\beta$ -L-arabinofuranosyl (1 $\rightarrow$ 3)]- $\beta$ -D-glucopyranoside (11) by intensive interpretation of spectral data.

**Key words:** *Helwingia chinensis*; Cornaceae; Fructofuranose; Flavonoids; Antibacterial activity

*Helwingia chinensis* Batal (Cornaceae) is distributed in the western and southern regions of China, for example, Gansu, Guizhou, Hubei, Hunan, Shanxi, Sichuan, Tibet and Yunnan (Song *et al.*, 1990). Its flowers and leaves were edible, and a decoction of the

leaves and the bark are ingested for treating skin inflammations (Zhonghua Bencao Bianweihui, 1999). The aerial part of this plant has long been used to treat dysentery, hematochezia, swelling, etc (How, 1997). Our previous investigation of the plant reported the iso-

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lation and characterization of three new triterpenoids (Lai *et al.*, 2003) and secoiridoid glycosides (Lai *et al.*, 2006). In continuation of our work on this genus, a new fructofuranose and ten known compounds were isolated from the EtOH extraction of the aerial part of *Helwingia chinensis*. Their structures were elucidated by intensive interpretation of spectral data.

## Results and Discussion

Compound **1** was isolated as an amorphous powder, showed the molecular formula  $C_{26}H_{28}O_{13}$  based on the  $[M-H]^+$  ion peak at  $m/z$  547 in the negative FAB mass spectrum (MS) and NMR spectral data, which was confirmed by negative high resolution (HR)-FAB mass experiment at  $m/z$  547.1438 ( $[M-H]^+$ ,  $C_{26}H_{27}O_{13}$ , calcd. 547.1643). 13 unsaturated degrees and its  $^{13}C$ -NMR data showed the presence of two phenyl groups in the structure of **1**. The  $^{13}C$ -NMR and DEPT experiments indicated the presence of two methoxys,

two methylenes, twelve methines and ten quaternary carbons. In the  $^1H$ -NMR spectrum (see Table 1) of **1**, a typical ABX aromatic proton system at  $\delta$  7.14 (1H, d,  $J = 8.4$  Hz), 7.23 (1H, dd,  $J = 8.4, 1.4$  Hz) and 7.43 (1H, d,  $J = 1.4$  Hz) and one *trans*-, -unsaturated olefin at  $\delta$  6.87, 8.01 (each 1H, d,  $J = 15.9$  Hz) were observed, which suggested the presence of a (*E*)-caffeoyl moiety. This was confirmed by the HMBC experiments based on the correlations of between at  $\delta$  8.01 and  $\delta$  123.6 (s, C-1), 111.4 (d, C-2), 115.4 (d, C-8), 167.9 (s, C=O) (see Figure. 2). Moreover, its  $^1H$ -NMR spectrum contained another set of signals of a *trans*-, -unsaturated olefin at  $\delta$  6.71, 8.12 (each 1H, d,  $J = 15.8$  Hz) and two aromatic proton signals at  $\delta$  7.13 (2H, s). The carbon signals at  $\delta$  166.9 (s), 149.3 ( $\times 2$ , s), 146.7 (d), 140.6 (s), 125.2 (s), 115.3 (d), 107.0 ( $\times 2$ , d), 56.5 ( $\times 2$ , q) showed the presence of 3, 5-dimethoxycoumaroyl group. This was confirmed

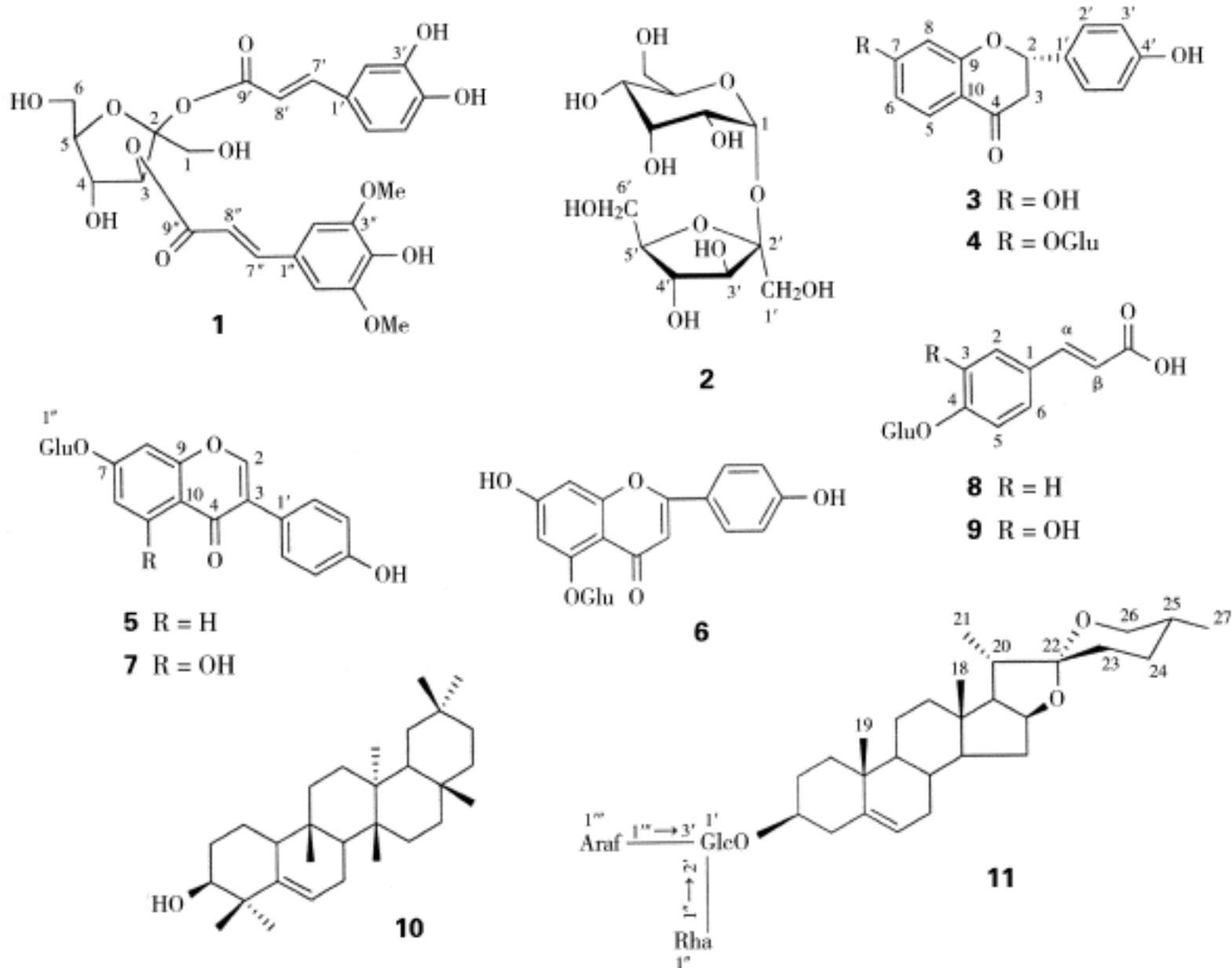


Fig. 1 The structures of compounds 1 - 11

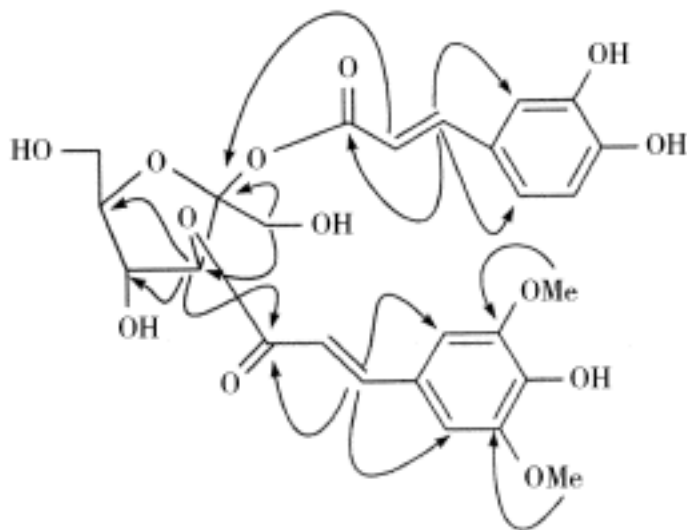


Fig. 2 Key HMBC Correlations of compound 1

by the HMQC and HMBC experiments based on the correlations at  $^1\text{H}$  3.86 (6H, s) with  $^{13}\text{C}$  149.3 ( $\times 2$ , s),  $^1\text{H}$  6.71 with  $^{13}\text{C}$  125.2 (s) (see Figure). Except the above mentioned evidences, six carbon signals were present at  $^{13}\text{C}$  105.0 (s), 84.9 (d), 79.6 (d), 74.2 (d), 65.9 (t), 63.5 (t). The presence of  $\beta$ -D-fructofuranose was identified by compared them with that of literature (Leslie *et al.*, 1980).

Long-rang correlations through  $^3J$  in the HMBC spectrum (See Figure 2) at  $^1\text{H}$  6.50 (1H, d,  $J = 7.7$  Hz, H - 3) with  $^{13}\text{C}$  166.9 (s, C = O) indicated that 3, 5-dimethoxycoumaroyl group located at C - 3. The weak correlations between at  $^1\text{H}$  6.87 (1H, d,  $J = 15.9$  Hz) with  $^{13}\text{C}$  105.0 (s) showed that (*E*)-caffeoyl moiety was located at C - 2. Based on above mentioned evidence, the structure of **1** was identified to be 2-*O*-(*E*)-caffeoyl-3-*O*-(3, 5-dimethoxyl)-(*E*)-coumaroyl- $\beta$ -D-fructofuranose.

Compounds **2** - **11** were elucidated to be 2-*O*- $\beta$ -D-fructofuranosyl- $\beta$ -D-allopyranose (**2**) (Hongh *et al.*, 1986), liquiritigenin (**3**) (Tsutomu *et al.*, 1985), 4-hydroxy-2, 3-dihydro-flavonone 7-*O*- $\beta$ -D-glucopyranoside (**4**) (Shul ts *et al.*, 2000), daidzin (**5**) (Park *et al.*, 1992), apigenin 5-*O*- $\beta$ -D-glucopyranoside (**6**) (Martin *et al.*, 1991), apigenin-7-*O*- $\beta$ -D-glucopyranoside (**7**) (Wang *et al.*, 1990), coumaric acid 4-*O*- $\beta$ -D-glucopyranoside (**8**) (Cui *et al.*, 1992), glucopyranosylcaffeic acid (**9**) (Cui *et al.*, 1992), 3-hydroxyglutin-5-ene (**10**) (Antonio *et al.*, 1987), diosgenin 3-*O*- $\beta$ -L-rhamnopyranosyl (1 2)-[ $\beta$ -L-arabinofuranosyl (1 3)]- $\beta$ -D-glucopyranoside (**11**) (Xu *et*

*al.*, 1988) by NMR spectra data and compared with the report in the literatures. By the paper diffusion method (5 mm diameter) to assay their activities of against *Shigella flexneri*, *S. dysenteriae*, *S. sonnei*, *Mycobacterium tuberculosis*,  $\alpha$ -Hemolytic streptococcus and *Streptococcus pneumoniae*, compounds **1** and **6** showed weak activities against *S. flexneri* and *M. tuberculosis* in agar diffusion assay, respectively. In this paper, we describe the structures elucidation by various NMR spectra analysis.

## Experimental

**General experimental procedures** Optical rotation was taken on a SEPA-300 polarimeter. FAB/MS data were obtained on a VG AutoSpec-3000 spectrometer.  $^1\text{H}$ -,  $^{13}\text{C}$ -, and 2D-NMR spectra were recorded on a Bruker AM 400 NMR and a DRX-500 spectrometer with TMS as internal standard. Silica gel (200 - 300 mesh, or silica gel H, 10 - 40  $\mu\text{m}$ ) for column chromatography (CC) and silica gel plate (GF254) for thin-layer chromatography (TLC) were obtained from the Qingdao Marine Chemical Factory, Qingdao, Shandong Province China.

**Plant material** The aerial parts of *Helwingia chinensis* were collected in Xishuangbanna, Yunnan, P. R. China in July 2002 (Lai *et al.*, 2003).

**Extraction and Isolation** The air-dried aerial parts (40 kg) were extracted twice with 95% EtOH at r. t. and the fractions were described as in the literature (Lai *et al.*, 2006). The fraction B was rechromatographed over silica gel (200 - 300 mesh), eluting with  $\text{CHCl}_3$  - MeOH (99 : 1 to 10 : 1) to afford compound **10** (32 mg). The fraction D (3.1 g) was purified by repeated CC on silica gel ( $\text{CHCl}_3$  - MeOH 50 : 1, 30 : 1, 20 : 1, 10 : 1) and then Sephadex LH-20 eluted by MeOH to give **1** (12 mg), **3** (16 mg) and **5** (24 mg). The fraction E (1.9 g) was purified by CC on silica gel;  $\text{CHCl}_3$  - MeOH 20 : 1 to 4 : 1) and then Sephadex LH-20 (MeOH) to give **4** (28 mg), **6** (38 mg) and **7** (57 mg). The BuOH extract (15 g) was fractionated by CC on silica gel (200 - 300 mesh),  $\text{CHCl}_3$  - MeOH from 20 : 1 to 2 : 1) and then RP-18 (MeOH- $\text{H}_2\text{O}$  6 : 4 to 8 : 2) to afford the compounds **2** (1.2 g), **8** (19 mg), **9** (325 mg) and **11** (14 mg).

**Antimicrobial activity assay** Inhibitory activities of compounds **1** - **11** against *Shigella flexneri*, *S. dysenteriae*, *S. sonnei*, *Mycobacterium tuberculosis*,  $\alpha$ -Hemolytic streptococcus and *Streptococcus pneumoniae* were determined by the paper disk diffusion assay on agar plates as described (Wang *et al.*, 2003). Only compounds **1** and **6** showed weak activities (6 mm disk) against *S. flexneri* and *M. tuberculosis*, respectively.

Table 1 The <sup>1</sup>H-, <sup>13</sup>C-NMR and 2D NMR spectral data of **1** in C<sub>5</sub>D<sub>5</sub>N (500 MHz and 125 MHz, in ppm)

No .	<sup>1</sup> H (Multiplicity, <i>J</i> in Hz)	<sup>13</sup> C	HMBC (H C)
1	4.32 (2H, s)	65.9 t	C-2, 3
2		105.0 s	
3	6.50 (1H, d, 7.7)	79.6 d	C-1, 2, 4, 9
4	5.46 (1H, t, 7.5)	74.2 d	C-2, 3, 5, 6
5	4.78 (1H, m)	84.9 d	C-4, 6
6	4.57 (1H, dd, 11.8, 3.9) 4.64 (1H, dd, 11.8, 4.8)	63.5 t	C-4, 5 C-4, 5
1		123.6 s	
2	7.43 (1H, s)	111.4 d	C-1, 3, 4, 6, 7
3		149.0 s	
4		151.1 s	
5	7.14 (1H, d, 8.4)	106.8 d	C-1, 3, 4
6	7.23 (1H, d, 8.4)	116.7 d	C-1, 2, 4, 5, 7
7	8.01 (1H, d, 15.9)	145.8 d	C-1, 2, 6, 8, 9
8	6.87 (1H, d, 15.9)	115.4 d	C-2, 1, 7, 9
9		167.9 s	
1		125.2 s	
2, 6	7.13 (2H, s)	107.0 d	C-1, 6 (2), 3, 4, 5, 7
3, 5		149.3 s	
4		140.6 s	
7	8.12 (1H, d, 15.8)	146.7 d	C-1, 2, 6, 8, 9
8	6.71 (1H, d, 15.8)	115.3 d	C-1, 7, 9
9		166.9 s	
OMe	3.86 (6H, s)	56.5 q	C-3, 5

**Chinenicside B (1)**: white powder, C<sub>26</sub>H<sub>28</sub>O<sub>13</sub>, negative FAB-MS *m/z* (%): 547 [M-H]<sup>-</sup> (100), 532 [M-16]<sup>+</sup> (23), 255 (46), 223 (18), 177 (17); negative HR-FAB-MS *m/z*: 547.1438 ([M-H]<sup>-</sup>, C<sub>26</sub>H<sub>27</sub>O<sub>13</sub>, calcd .547.1643); <sup>1</sup>H-NMR and <sup>13</sup>C-NMR (see table 1).

**2-O- -D-fructofuranosyl- -D-allopyranose (2)**: white powder, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, negative FAB-MS *m/z* (%): 341 [M-H]<sup>-</sup> (100), 293 (7), 127 (12); <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 400 MHz): 5.20 (1H, d, *J*=10.6 Hz, H-1), 5.07 (1H, d, *J*=10.6 Hz, H-1), 5.15 (1H, d, *J*=3.7 Hz, H-1), 4.81 (1H, dd, *J*=5.3, 11.9 Hz, H-6), 4.42 (1H, dd, *J*=2.0, 11.9 Hz, H-6), 4.77 (1H, d, *J*=10.2 Hz, H-6), 4.52 (1H, d, *J*=10.2 Hz, H-6); <sup>13</sup>C-NMR (CD<sub>3</sub>OD, 100 MHz): 62.1 (t, C-1), 104.1 (s, C-2), 77.0 (d, C-3), 74.3 (d, C-4), 82.6 (d, C-5), 62.2 (t, C-6), 91.8 (d, C-1), 71.7 (d, C-2), 72.9 (×2, d, C-3, 5), 69.8 (d, C-4), 60.5 (t, C-6).

**Liquiritigenin (3)**: yellow powder, C<sub>15</sub>H<sub>12</sub>O<sub>4</sub>, EI-MS *m/z* (%): 256 [M]<sup>+</sup> (100), 239 (7), 228 (12), 163 (17), 145 (22), 137 (73), 121 (95), 110 (41), 101 (55), 85 (40), 55 (70); <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD): 2.75 (1H, dd, *J*=2.8, 16.9 Hz, H-3), 3.25 (1H, dd, *J*=13.6, 16.5 Hz, H-3), 5.55 (1H, dd, *J*=2.8, 13.0 Hz, H-2),

6.80 (1H, d, *J*=2.0 Hz, H-8), 6.88 (1H, dd, *J*=2.0, 8.8 Hz, H-6), 7.21 (2H, br. d, *J*=8.6 Hz, H-3, 5), 7.53 (2H, br. d, *J*=8.7 Hz, H-2, 6), 8.16 (1H, d, *J*=8.8 Hz, H-5); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD): 190.4 (s, C-4), 166.5 (s, C-7), 164.5 (s, C-9), 159.3 (s, C-4), 130.2 (s, C-1), 129.5 (d, C-5), 128.7 (×2, d, C-2, 6), 116.5 (×2, d, C-3, 5), 114.9 (s, C-10), 111.5 (d, C-6), 103.7 (d, C-8), 80.3 (d, C-2), 44.4 (t, C-3).

**4-Hydroxy-2,3-dihydroflavonone 7-O-β-D-glucoside (4)**: yellow powder, C<sub>21</sub>H<sub>22</sub>O<sub>9</sub>, negative FAB-MS *m/z* (%): 417 [M-H]<sup>-</sup> (64), 403 (16), 385 (5), 357 (8), 325 (100), 311 (978), 293 (12), 265 (17), 156 (4), 80 (14); <sup>1</sup>H-NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N) ppm: 5.54 (1H, dd, *J*=2.8, 12.9 Hz, H-2), 2.94 (1H, dd, *J*=2.8, 16.6 Hz, H-3), 3.22 (1H, dd, *J*=13.0, 16.6 Hz, H-3), 8.20 (1H, d, *J*=8.7 Hz, H-5), 6.94 (1H, dd, *J*=2.0, 8.7 Hz, H-6), 6.85 (1H, d, *J*=2.2 Hz, H-8), 7.52 (2H, d, *J*=8.7 Hz, H-2, 6), 7.40 (2H, d, *J*=8.7 Hz, H-3, 5), 5.70 (1H, d, *J*=7.4 Hz, H-1), 4.58 (1H, *J*=11.8 Hz, H-6), 4.34-4.44 (4H, m); <sup>13</sup>C-NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N) ppm: 190.2 (s, C-4), 166.7 (s, C-7), 164.5 (s, C-9), 158.9 (s, C-4), 133.4 (s, C-1), 129.5 (d, C-5), 128.3 (×

2, d, C-2, 6), 117.5 ( $\times 2$ , d, C-3, 5), 114.5 (s, C-10), 111.8 (d, C-6), 80.2 (d, C-2), 44.8 (t, C-3), 102.2 (d, C-1), 78.9 (d, C-3), 78.6 (d, C-5), 74.9 (d, C-2), 71.5 (d, C-4), 62.5 (t, C-6).

**Daidzin (5)**: white powder,  $C_{21}H_{20}O_9$ , negative FAB-MS  $m/z$  (%): 569  $[M+154]^-$  (100), 415  $[M-H]^-$  (15), 253  $[M-162]^-$  (45);  $^1H$ -NMR (500 MHz,  $CD_3OD$ ): 8.36 (1H, dd,  $J=3.1, 8.2$  Hz, H-3, 5), 8.14 (1H, dd,  $J=3.1, 8.2$  Hz, H-2, 6), 7.78 (1H, dd,  $J=2.9, 8.1$  Hz, H-5), 7.43 (1H, s, H-2), 7.29 (1H, dd,  $J=2.6, 8.2$  Hz, H-6), 5.82 (1H, d,  $J=7.2$  Hz, H-1), 4.62 (2H, d,  $J=11.9$  Hz, H-6), 4.27-4.45 (3H, m), 4.26 (1H, br s);  $^{13}C$ -NMR (125 MHz,  $CD_3OD$ ): 175.8 (s, C-4), 162.4 (s, C-7), 159.2 (s, C-9), 157.9 (s, C-4), 153.0 (d, C-2), 131.1 (d, C-2, 6), 127.9 (d, C-5), 125.2 (s, C-1), 119.3 (s, C-10), 116.4 (d, C-3, 5), 116.1 (d, C-6), 104.3 (d, C-8), 101.9 (d, C-1), 79.3 (d, C-3), 78.5 (d, C-5), 74.9 (d, C-2), 71.3 (d, C-4), 62.5 (t, C-6).

**Apigenin 5-O- $\beta$ -D-glucopyranoside (6)**: white powder,  $C_{21}H_{20}O_{10}$ , negative FAB-MS  $m/z$  (%): 431  $[M-H]^-$  (100), 405 (8), 282 (13), 215 (17), 145 (24);  $^1H$ -NMR (500 MHz,  $CD_3OD$ ) ppm: 7.88 (1H, d,  $J=8.6$  Hz, H-2, 6), 7.20 (1H, d,  $J=6.1$  Hz, H-3, 5), 7.11 (1H, d,  $J=1.2$  Hz, H-8), 6.91 (1H, s, H-3), 6.86 (1H, d,  $J=1.5$  Hz, H-6), 5.86 (1H, d,  $J=7.4$  Hz, H-1), 4.58 (2H, d,  $J=10.6$  Hz, H-6), 4.44-4.34 (3H, m), 4.23 (1H, br s);  $^{13}C$ -NMR (125 MHz,  $CD_3OD$ ) ppm: 182.9 (s, C-4), 165.0 (s, C-5), 164.1 (s, C-7), 162.9 (s, C-9), 162.6 (s, C-2), 157.9 (s, C-4), 129.0 (d, C-3, 5), 122.1 (s, C-1), 116.9 (d, C-2, 6), 106.6 (s, C-10), 104.1 (d, C-3), 100.7 (d, C-6), 95.4 (d, C-8), 101.8 (1d, C-1), 79.3 (d, C-3), 78.5 (d, C-5), 74.9 (d, C-2), 71.2 (d, C-4), 62.4 (t, C-6).

**Apigenin-7-O- $\beta$ -D-glucoside (7)**: white powder,  $C_{21}H_{20}O_{10}$ , negative FAB-MS  $m/z$  (%): 431  $[M-H]^-$  (100), 415 (11), 269  $[M-162]^-$  (70);  $^1H$ -NMR (400 MHz,  $CD_3OD$ ): 8.11 (1H, s, H-2), 7.70 (2H, d,  $J=8.5$  Hz, H-3, 5), 7.28 (2H, d,  $J=8.5$  Hz, H-2, 6), 6.94 (1H, d,  $J=2.7$  Hz, H-8), 6.86 (1H, d,  $J=2.7$  Hz, H-6), 5.81 (1H, d,  $J=7.3$  Hz, H-1), 4.57 (2H, d,  $J=11.8$  Hz, H-6), 4.44-4.34 (3H, m), 4.20 (1H, br s);  $^{13}C$ -NMR (100 MHz,  $CD_3OD$ ): 181.4 (s, C-4), 164.4 (s, C-7), 159.4 (s, C-5), 158.1 (s, C-4), 163.0 (s, C-9), 153.9 (s, C-2), 131.0 (d, C-2, 6), 122.1 (s, C-1), 116.4 (d, C-3, 5), 107.3 (s, C-10), 100.7 (d, C-6), 95.2 (d, C-8), 100.7 (d, C-6), 101.7 (d, C-1), 79.3 (d, C-3), 78.5

(d, C-5), 74.8 (d, C-2), 71.2 (d, C-4), 62.4 (t, C-6).

**Coumaric acid-4-O- $\beta$ -D-glucopyranoside (8)**: white powder,  $C_{15}H_{18}O_8$ , negative FAB-MS  $m/z$  (%): 325  $[M-H]^-$  (100), 163 (27);  $^1H$ -NMR (400 MHz,  $C_5D_5N$ ): 7.30 (2H, d,  $J=8.6$  Hz, H-2, 6), 6.71 (2H, d,  $J=8.6$  Hz, H-3, 5), 7.75 (1H, d,  $J=15.9$  Hz, H-), 6.30 (1H, d,  $J=15.9$  Hz, H-), 5.64 (1H, d,  $J=7.8$  Hz, H-1), 4.54 (1H, d,  $J=10.5$  Hz, H-6), 4.42-4.26 (4H, m);  $^{13}C$ -NMR (100 MHz,  $C_5D_5N$ ): 170.5 (s, CO), 159.7 (s, C-4), 143.2 (d, C-), 130.5 ( $\times 2$ , d, C-2, 6), 127.5 (s, C-1), 117.8 (d, C-), 116.5 ( $\times 2$ , d, C-3, 5), 103.6 (d, C-1), 79.2 (d, C-3), 78.4 (d, C-5), 74.9 (d, C-2), 71.1 (d, C-4), 62.2 (t, C-6).

**Glucopyranosylcaffeic acid (9)**: white powder,  $C_{15}H_{18}O_9$ , negative FAB-MS  $m/z$  (%): 341  $[M-H]^-$  (100), 324 (11), 179 (26);  $^1H$ -NMR (400 MHz,  $C_5D_5N$ ): 8.04 (1H, d,  $J=15.9$  Hz, H-), 7.62 (1H, d,  $J=1.7$  Hz, H-2), 7.53 (1H, d,  $J=8.3$  Hz, H-5), 7.11 (1H, dd,  $J=1.6, 8.3$  Hz, H-6), 6.87 (1H, d,  $J=15.9$  Hz, H-), 5.62 (1H, d,  $J=7.7$  Hz, H-1), 4.52 (1H, d,  $J=10.2$  Hz, H-6), 4.42-4.26 (4H, m);  $^{13}C$ -NMR (100 MHz,  $C_5D_5N$ ): 169.7 (s, CO), 149.9 (s, C-3), 148.6 (s, C-4), 144.4 (d, C-), 130.9 (s, C-1), 120.9 (d, C-2), 118.9 (d, C-5), 116.5 (d, C-), 103.6 (d, C-1), 79.2 (d, C-3), 78.4 (d, C-5), 74.9 (d, C-2), 71.1 (d, C-4), 62.2 (t, C-6).

**3-Hydroxyglutin-5-ene (10)**: white powder,  $C_{30}H_{50}O$ , EI-MS  $m/z$  (%): 426  $[M]^+$  (18), 408 (21), 393 (5), 274 (100), 259 (57), 245 (9), 205 (28), 173 (23), 119 (43), 109 (54), 95 (72), 69 (84), 55 (75);  $^1H$ -NMR (400 MHz,  $CDCl_3$ ): 1.07, 1.04, 1.00, 0.95, 0.91, 0.90, 0.86, 0.82, 0.81, 0.76 (each, 3H, s), 3.37 (1H, br s, H-3), 5.52 (1H, d,  $J=4.8$  Hz, H-5);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ ): 18.1 (t, C-1), 27.7 (t, C-2), 76.1 (d, C-3), 40.5 (s, C-4), 141.6 (s, C-5), 121.6 (d, C-6), 23.4 (t, C-7), 47.3 (d, C-8), 34.6 (s, C-9), 49.6 (d, C-10), 32.9 (t, C-11), 30.2 (C-12), 37.7 (s, C-13), 39.1 (s, C-14), 34.5 (t, C-15), 34.9 (t, C-16), 29.9 (s, C-17), 42.9 (d, C-18), 34.9 (t, C-19), 28.1 (s, C-20), 31.9 (t, C-21), 39.1 (t, C-22), 28.8 (q, C-23), 25.2 (q, C-24), 16.0 (q, C-25), 18.1 (q, C-26), 18.2 (q, C-27), 32.2 (q, C-28), 31.9 (q, C-29), 34.3 (q, C-30).

**Diosgenin 3-O- $\beta$ -L-rhamnopyranosyl (1 $\rightarrow$ 2)-[ $\beta$ -L-arabinofuranosyl (1 $\rightarrow$ 3)]- $\beta$ -D-glucopyranoside (11)**: white powder,  $C_{44}H_{70}O_{16}$ , negative FAB-MS  $m/z$  (%): 853  $[M-$

H] (100), 721 (14), 691 (18), 479 (11), 447 (24), 411 (39); <sup>1</sup>H-NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N) : 6.30 (1H, br s, H-1), 5.31 (1H, d, *J* = 4.7 Hz, H-6), 4.98 (1H, d, *J* = 3.7 Hz, H-1), 4.96 (1H, d, *J* = 5.7 Hz, H-1), 3.59 (1H, br d, *J* = 10.7 Hz, H-26), 3.51 (1H, dd, *J* = 10.7, 10.8 Hz, H-26), 4.63 (1H, dd, *J* = 3.3, 9.3 Hz, H-3), 1.78 (3H, d, *J* = 6.3 Hz, H-6), 1.14 (1H, d, *J* = 6.9 Hz, H-21), 1.05 (3H, s, H-19), 0.83 (3H, s, H-18), 0.70 (3H, d, *J* = 5.0 Hz, H-27); <sup>13</sup>C-NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N) : 37.6 (t, C-1), 31.9 (t, C-2), 77.8 (d, C-3), 39.9 (t, C-4), 140.8 (s, C-5), 121.9 (d, C-6), 32.3 (t, C-7), 31.7 (d, C-8), 50.3 (d, C-9), 37.2 (s, C-10), 21.2 (t, C-11), 39.0 (t, C-12), 40.5 (s, C-13), 56.7 (d, C-14), 30.2 (t, C-15), 81.2 (d, C-16), 62.9 (d, C-17), 19.5 (q, C-18), 16.4 (q, C-19), 42.0 (d, C-20), 15.1 (q, C-21), 109.3 (s, C-22), 32.4 (t, C-23), 29.3 (t, C-24), 30.7 (d, C-25), 66.9 (t, C-26), 17.4 (q, C-27), Glc: 100.2 (C-1), 78.1 (C-2), 77.9 (C-3), 76.8 (C-4), 77.0 (C-5), 62.6 (C-6), Rha: 102.0 (C-1), 72.6 (C-2), 72.9 (C-3), 74.2 (C-4), 69.6 (C-5), 18.7 (C-6), Ara: 109.7 (C-1), 82.8 (C-2), 77.5 (C-3), 86.7 (C-4), 61.4 (C-5).

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